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SiC Dopant Incorporation Control Using Site-Competition CVD

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The use of site-competition epitaxy, which is based on intentional variation of the Si/C ratio during epitaxy, has now been reproduced in numerous national and international laboratories. Presented in this paper is a summary of the site-competition technique as a comparison of controlled doping on C-face 6H-SiC(000 $\bar{1}$) versus Si-face 6H-SiC(0001) substrates for phosphorous (P), aluminum (Al), boron (B), and nitrogen (N). Also reported herein is the detection of hydrogen in boron-doped CVD SiC epilayers and hydrogen-passivation of the boron-acceptors. Results from low temperature photoluminescence (LTPL) spectroscopy indicate that the hydrogen content increased as the C - V measured net hole concentration increased. Secondary ion mass spectrometry (SIMS) analysis revealed that the boron and the hydrogen incorporation both increased as the Si/C ratio was sequentially decreased within the CVD reactor during epilayer growth. Boron-doped epilayers that were annealed at 1700 °C in argon no longer exhibited hydrogen-related LTPL lines, and subsequent SIMS analysis confirmed the outdiffusion of hydrogen from the boron-doped SiC epilayers. The C - V measured net hole concentration for the B-doped epitaxial layers increased more than three-fold as a result of the 1700 °C anneal, which is consistent with hydrogen passivation of the boron-acceptors. For N-doped epitaxy, N incorporation into C-sites is favored on the Si-face whereas N incorporation into the Si-site is apparently the preferred lattice site on the C-face. Both P and N exhibit preferred incorporation on the C-face while Al and B incorporation is more efficient on the Si-face.

1. Introduction

In order to ensure reproducible and reliable SiC semiconductor device characteristics, controlled dopant incorporation must be accomplished. Unlike the doping technology routinely used in the silicon semiconductor industry, it is well known that SiC cannot be efficiently doped by diffusion at typical SiC epitaxial growth temperatures. Doping of SiC epitaxial layers of a device structure is accomplished in situ during the crystal growth of each epitaxial layer by flowing either a specific p-type or n-type dopant source into the CVD reactor. The most common p-type sources are trimethylaluminum (TMA) and diborane (B_2H_6) for obtaining Al-doped and B-doped SiC, respectively. Nitrogen (N_2) is the most common n-type dopant whereas phosphorus-doping (using PH_3) for producing n-type SiC epitaxial layers is less common. However, control over net dopant incorporation for CVD SiC epilayers by simply increasing or decreasing dopant-source flow (i.e. reactor concentration of dopant species) during epitaxial layer growth is limited both in reproducibility and in attainable doping range. This doping range was typically limited between $N_D \cong 2 \times 10^{16}$ to $5 \times 10^{18} \text{ cm}^{-3}$ for n-type and from $N_A \approx 2 \times 10^{16} \text{ cm}^{-3}$ to $1 \times 10^{18} \text{ cm}^{-3}$ for p-type 6H-SiC epilayers [1].

Both the reproducibility and doping range has been greatly improved with the discovery of the site-competition epitaxial technique [2], which is based on varying the

Si-source to C-source ratio (Si/C ratio) within the crystal growth reactor to control the dopant incorporation during SiC epitaxial layer (epilayer) growth. Control of dopant incorporation is accomplished by varying the Si/C ratio within the growth reactor to effectively exclude or enhance a particular dopant atom from either a Si lattice site (Si-site) or C lattice site (C-site) of the growing SiC epilayer. As previously reported [3], the proposed mechanism for site-competition epitaxy on 6H-SiC(0001) Si-face substrates is based on the experimental evidence that Al dopant incorporation is inversely related to the Si/C ratio, whereas the N dopant incorporation is directly related to the Si/C ratio within the reactor during epilayer growth. Site-competition epitaxy has been reported for control of nitrogen, phosphorus, aluminum, and boron dopant incorporation for the CVD of SiC(0001) Si-face and C-face epilayers [2 to 5]. The use of this technique has also been reproduced on SiC(0001) Si-face substrates in other laboratories using either propane [6, 7] or methane [8] in atmospheric and low pressure CVD systems, as well as reproduced [9] on SiC(1 $\bar{2}$ 10) a-face substrates. Use of this technique has enabled an expansion of the reproducible doping ranges to include decreased concentrations ($N_D < 1 \times 10^{14} \text{ cm}^{-3}$) for the fabrication of multi-kilovolt SiC power devices, whereas the availability of greater doping concentrations ($N_D > 5 \times 10^{19} \text{ cm}^{-3}$) has resulted in devices with increased performance because of lower parasitic resistances. For example, use of site-competition epitaxy has led to improved device performance which includes the first multi-kilovolt rectifiers [10], ohmic as deposited contacts [11], and high temperature JFETs [12].

2. Experimental

The 6H-SiC epilayers were grown on commercially available n-type 6H- and 4H-(0001)SiC Si-face and C-face 6H-(000 $\bar{1}$)SiC boulev-derived wafers [13] in an atmospheric pressure CVD system [14, 15], with a typical growth rate of 3 to 4 $\mu\text{m/h}$. The SiC substrates were pre-cleaned using a standard degreasing solution, followed by immersion in boiling sulfuric acid for 10 min, with a final deionized-water rinse and then dried with filtered nitrogen. The cleaned substrates were placed onto a SiC-coated graphite susceptor and then loaded into a water-cooled fused-silica reactor using a fused-silica-carrier. The samples were heated via the RF-coupled susceptor which was temperature controlled at 1500 $^{\circ}\text{C}$ using an optical pyrometer. Silane (gas cylinder containing 3% in H_2) and propane (3% in H_2) were used with a 3 sLpm flow of H_2 carrier/co-reactant for SiC epilayer growth. A flow of ultrapure hydrogen chloride gas (90 sccm) in a 3 sLpm flow of hydrogen was used during a 1350 $^{\circ}\text{C}$ in situ etch just prior to epilayer growth. All gases were mass flow controlled, including the ultra-pure hydrogen carrier-gas which was purified by using a heated-palladium diffusion cell. The epilayers were doped n-type by the addition of phosphine (200 ppm PH_3 in H_2) or nitrogen (0.1% N_2 in H_2) and p-type by the addition of diborane (100 ppm B_2H_6 in H_2) or trimethylaluminum (bubbler configuration) into the reactor during epilayers growth. Secondary ion mass spectrometry (SIMS) was performed [16] using a CAMECA IMS-4f double-focussing, magnetic sector ion microanalyzer. Cesium bombardment was used for determination of hydrogen, boron, phosphorous, and nitrogen atomic concentration profiles by using the detector in a negative secondary ion detection mode to monitor H-, P- and the diatomic species B(+C)-, N(+C)-, respectively. The aluminum and higher accuracy boron elemental concentrations were determined by using oxygen bombardment and a positive secondary

ion detection mode. The sputter-time data was converted into depth data by measurement of crater depths, by using a stylus profilometer. Capacitance–voltage (C – V) measurements for B-doped epitaxial layers were obtained at 100 kHz on a mercury-probe instrument with a mercury-Schottky (contact area = $1.64 \times 10^{-3} \text{ cm}^2$), using the mechanical sample-hold-down paddle as the electrical ground on the back of the sample. The low temperature photoluminescence (LTPL) was performed at 2K by immersing the SiC samples in pumped liquid helium, and excited using the 3250 Å radiation from a He–Cd laser. The LTPL spectra were recorded on a 0.75 meter Spex monochromator (10 Å/mm), using a thermoelectrically cooled ($-30 \text{ }^\circ\text{C}$) GaAs/CsO photomultiplier and a photon counting system.

3. Site-Competition Epitaxial CVD

As already stated, the Si/C ratio within the growth reactor has a strong influence on intentional and unintentional dopant incorporation during the epitaxial CVD growth of 6H, 3C (on 6H), 15R, and 4H-SiC. Specifically, the active n-type (nitrogen) carrier concentration was found to be directly proportional to the Si/C ratio, whereas, the active p-type (aluminum) concentration was found to be inversely proportional to the Si/C ratio for epitaxial growth on the SiC(0001)Si-face basal plane. For example, as the Si/C ratio within the growth reactor was decreased by increasing the propane flow, the active nitrogen concentration in the subsequently grown SiC epitaxial layers decreased. When the Si/C ratio was decreased from Si/C = 0.44 to 0.1, the unintentionally doped epitaxial layers changed from n-type to p-type. As a result, both p-type and n-type epilayers have been produced with room temperature carrier concentrations of $< 1 \times 10^{14} \text{ cm}^{-3}$, as measured by both mercury-probed C – V and LTPL [17]. Previously, the unintentionally doped epilayers produced in our laboratory were exclusively n-type with the lowest net carrier concentrations typically limited to about $n = 2 \times 10^{16} \text{ cm}^{-3}$.

Dopants in SiC are believed to occupy specific lattice sites, specifically nitrogen occupies the carbon site (C-site) while aluminum (Al) occupies the silicon site (Si-site) of the SiC lattice [18, 19]. Based upon this information, and on our experimental results of decreasing the Si/C ratio, the relative increase in C concentration is proposed to “out-compete” the N for the C-sites of the growing SiC lattice. The analogous situation exists for an increased Si/C ratio, in which the relative increase in Si concentration “outcompetes” the Al for the Si-sites of the growing SiC lattice. This model has been previously named “site-competition epitaxy” and was initially used to rationalize the experimental results of active dopant dependence on the Si/C ratio. For example, a N_2 flow resulting in a reactor concentration of 100 ppm of N was introduced into the growth reactor where the majority of the N was excluded from the growing epilayer by only decreasing the Si/C ratio from about Si/C = 0.44 to 0.1. Subsequent experiments using a Si/C = 0.1 with a 100 ppm of N resulted in consistently producing an intentionally N-doped n-type SiC epilayer with a net carrier concentration of $n = 1 \times 10^{15} \text{ cm}^{-3}$. In contrast, growth using the more typical Si/C = 0.44 with 100 ppm of N yields an n-type epilayers of $n = 2 \times 10^{17} \text{ cm}^{-3}$. For the epilayers grown using a Si/C = 0.1 ($n = 1 \times 10^{15} \text{ cm}^{-3}$), the increased amount of C is believed to have outcompeted the N for the C-sites of the growing SiC lattice.

To determine if the electrically measured results corresponded to actual atomic N incorporation, a series of N doping profiles were grown and then characterized using

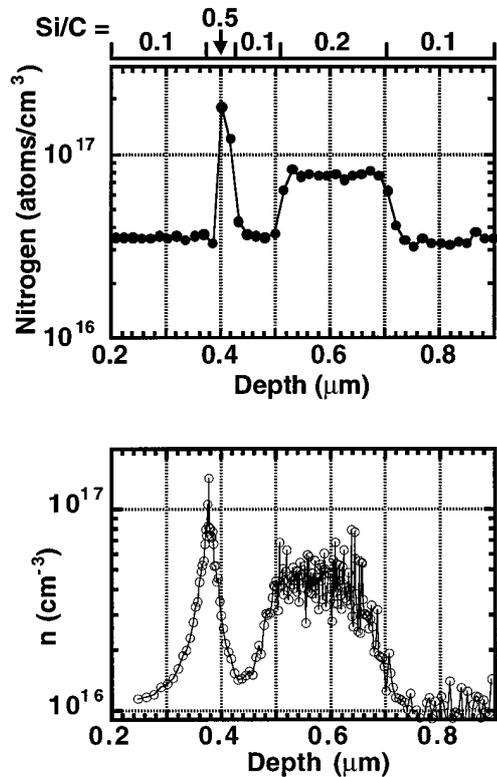


Fig. 1. A direct comparison between a SIMS profile analysis (top) and a mercury-probe $C-V$ electrical result for a sample grown by varying only the carbon-source concentration (400 to 1800 at. ppm) while maintaining a constant silicon-source concentration (200 at. ppm) and a constant nitrogen concentration (180 at. ppm) within the CVD reactor during SiC epilayer growth

mercury-probe $C-V$ and SIMS. During the growth of n-type doped epilayers, the silane (200 ppm) and molecular nitrogen (90 ppm) concentrations were held constant while only the propane concentration was varied between 130 and 660 ppm. The N dopant profiles were then characterized using SIMS and mercury-probe $C-V$. The results from one such experiment are shown in Fig. 1. The SIMS profile (Fig. 1 top) exhibits variations of atomic N concentration within the grown epilayer from varying only the Si/C ratio (between 0.5 and 0.1) during

epilayer growth. The net carrier concentration profile obtained from mercury-probe $C-V$ for the same sample (bottom of Fig. 1) correlates well with the SIMS profile. These results indicate that site-competition epitaxy can be used to control N-dopant incorporation into electrically active crystal sites of the growing SiC epilayer. To date, use of the site-competition epitaxial technique has been reported for control of phosphorus (P), Al, boron (B), and N dopant incorporation for the CVD of SiC(0001) Si-face and C-face epilayers of the various polytypes including 6H, 4H, 15R and 3C grown on 6H (3C/6H) [2, 3].

The remainder of the discussion of the site-competition effect is organized into sections for each specific dopant atom. This organization facilitates discussions of peculiarities associated with each dopant atom, such as the co-incorporation and hole passivation effect of hydrogen for B, the apparent reversal in site preference for N on the Si-face (C-sites) versus the C-face (Si-site), and the significant difference in dopant incorporation efficiency for each dopant atom when simultaneously incorporated into Si-face versus adjacent C-face SiC epilayers. Also for the following sections, 6H-SiC is referenced for clarity and serves only as an example because the other common polytypes (i.e. 4H, 15R, and 3C/6H) exhibit similar dopant incorporation behavior to the site-competition effect.

4. Phosphorus Doping

Phosphorus doping was studied to provide more data on the site-competition effect. This is because phosphorus presently appears to have limited interest as a potential

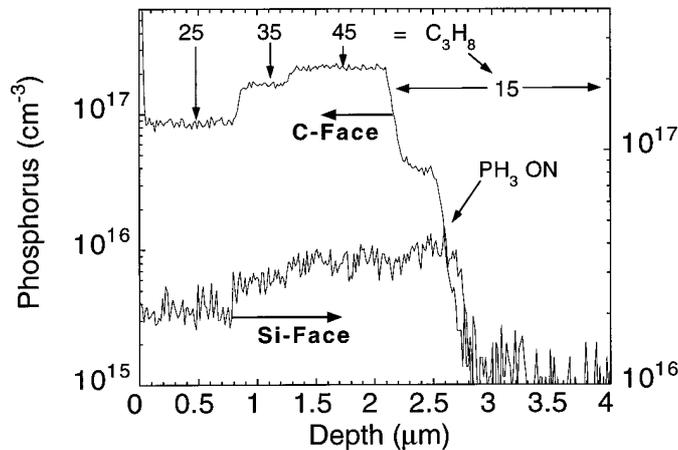


Fig. 2. SIMS depth profile of a phosphorus-doped epilayer simultaneously grown on a 6H-SiC(0001) Si-face versus a C-face substrate. Initially, the propane flow is constant then the phosphine flow is established. Then both the silane (20 sccm) and phosphine (100 sccm) flows are maintained constant while the propane flow is varied (stepwise)

replacement for nitrogen, especially considering that the phosphorus donor is reported to have only a slightly lower ionization energy (80 and 110 meV) [20] compared to that of the nitrogen donor (82 and 140 meV) [21] in 6H-SiC. For n-type doping with P, the site-competition effect is most consistent with the P atom mainly occupying the Si-sites. The P dopant incorporation was determined to be inversely related to the Si/C ratio as displayed in Fig. 2. As the propane flow was decreased, while maintaining a constant silane (20 sccm) and phosphine (100 sccm) flow, the SIMS determined P incorporation also decreased within the Si-face 6H-SiC epilayer. These changes in P incorporation with variation in the Si/C ratio are consistent with the P atom occupying the Si-sites of the SiC crystal lattice. As the propane flow is increased, the amount of vacant Si-sites increases which could allow enhanced P incorporation into the SiC epilayer.

Site-competition epitaxy had a pronounced effect for control of P dopant incorporation on both C-face and Si-face epilayers. As the propane flow was decreased, the P incorporation also decreased (see Fig. 2). As the silane flow was increased and then decreased, the P incorporation decreased then increased, respectively (not shown). It is believed that P is competing with Si for available Si-sites on the growing C-face SiC epilayer. This effect can be rationalized by considering that the lattice site occupied by each dopant atom is partly determined by the size of the dopant atom as compared to the size of the Si or C atom. Specifically, the non-polar covalent radii for the elements of interest are: Si (1.17 Å); C (0.77 Å); Al (1.26 Å); B (0.82 Å); P (1.10 Å); and N (0.74 Å); [22]. Using atomic size as a first approximation (i.e. by neglecting chemical bonding arguments), P should substitute for Si and not for C in the SiC lattice, which is consistent with our experimental results.

5. Aluminum and Boron Doping

It was previously reported [3] that the concentration of Al dopant atoms incorporated into a growing SiC epilayer can be decreased by increasing the silane concentration so

that Si outcompetes Al for the Si-sites. For comparison, two different experiments that were conducted used identical flows of TMA introduced into the reactor but employed different Si/C ratios during epilayer growth. The resulting p-type epilayer grown with a Si/C ratio of 0.44 was measured by C - V mercury probe to be $5 \times 10^{16} \text{ cm}^{-3}$, while the epilayer grown using a Si/C ratio of 0.11 yielded a degenerately doped p-type epilayer with an estimated net carrier concentration of $1 \times 10^{19} \text{ cm}^{-3}$. These experimental results support the hypothesis that as the Si/C ratio is decreased from 0.44 to 0.1, the relative amount of Si competing with the Al for the Si-sites of the SiC lattice also decreases, which results in an increased Al incorporation.

The site-competition effect remains active even at such highly degenerate Al dopant levels (i.e. although this effect is significantly diminished compared to the orders of magnitude change observed at lower dopant concentrations). As clearly demonstrated in Fig. 3, the concentration of Al incorporated into a growing SiC epilayer can be increased by decreasing only the Si/C ratio within the reactor during epilayer growth. This is accomplished by either increasing the C-source concentration (i.e. by increasing the propane flow into the reactor) or by decreasing the Si-source concentration in the CVD reactor. In Fig. 3, the SIMS determined Al incorporation increased as the propane flow was increased and also when the silane flow was decreased within the CVD reactor, which clearly demonstrates competition between Si and Al for the Si-sites on the growing Si-face 6H-SiC epilayer.

In general, p-type doping of epilayers grown on the C-face 6H-SiC(000 $\bar{1}$) samples was similar to that determined for the Si-face substrates. Both Al and B dopant incorporation on the C-face exhibited a similar dependence on the Si/C ratio, as previously described for the Si-face substrates. However, both Al and B incorporation

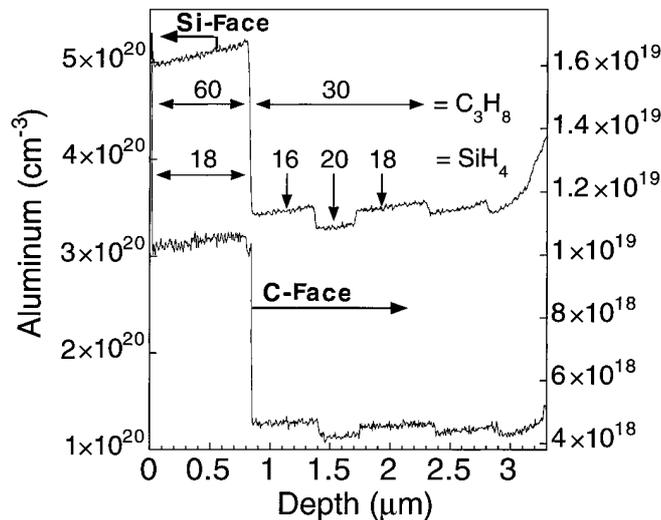


Fig. 3. SIMS depth profile of an aluminum-doped epilayer simultaneously grown on a 6H-SiC(0001) Si-face versus a C-face substrate. As the silane flow is varied during a constant propane flow, the Al is outcompeted by Si for available Si-sites. As the propane flow is increased to 60 sccm, Al incorporation increases because of the increase in available Si-sites

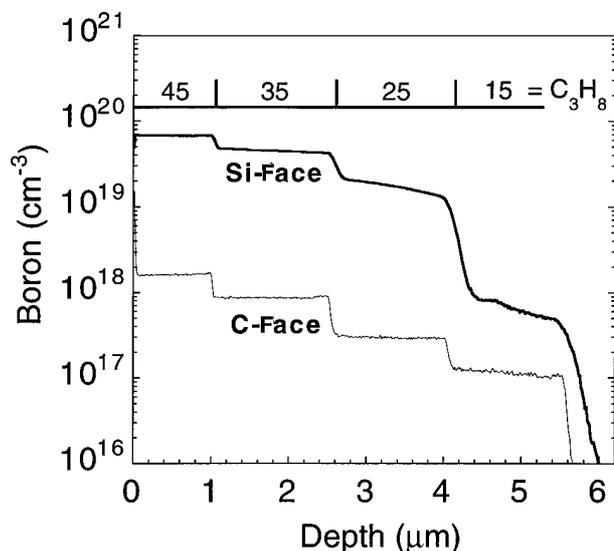


Fig. 4. SIMS depth profile of a boron-doped Si-face vs. C-face 6H-SiC(0001) epilayer from the same growth run. The silane (20 sccm) and diborane (50 sccm) flows were maintained constant as the propane flow was varied (sccm) during the epilayer growth

were markedly less efficient on the C-face substrates when compared to Si-face substrates that were doped during the same growth run. For Al doped C-face epilayers, the SIMS determined Al dopant incorporation was approximately 50× less than that of the corresponding Si-face epilayer. Similarly, B-doped C-face epilayers also exhibited a 50× lower atomic B concentration compared to simultaneously B-doped Si-face epilayers (see Fig. 4).

The similar behavior of B to Al is somewhat unexpected because B has been reported to occupy both the Si-site and the C-site [19, 23 to 26], which would preclude effective use of site-competition epitaxy for control of B doping in SiC. However, previous experimental results support that B preferentially occupies the Si-site of the SiC lattice [4, 26]. This is because B incorporation into the SiC epilayer decreases as the silane concentration increases (i.e. increasing the Si/C ratio), which is consistent with the increased amount of Si outcompeting the B for available Si-sites during growth of the SiC epilayer.

Conversely, boron incorporation can be increased by decreasing the Si/C ratio by decreasing the silane concentration or, alternatively, increasing only the propane concentration. Varying only the propane concentration for effective control of the boron doping is illustrated in Fig. 4, in which the Si/C ratio was decreased stepwise during epilayer growth by successive increases in propane flow while maintaining a constant silane (200 at. ppm) and diborane (3.3 at. ppm) concentration. Here, the boron incorporation in the epilayer increases as the propane concentration is increased because of the relative decrease in the Si/C ratio within the growth reactor. This relative decrease in silicon concentration enables the boron atoms to outcompete the silicon atoms for more of the available Si-sites on the surface of the growing SiC epilayer, resulting in increased boron incorporation.

To determine the reproducibility of the doping control, numerous B-doped SiC epilayers were grown during separate 2 h growth experiments, each using a constant Si/C

ratio ranging from Si/C = 0.1 to 0.5. For selected epilayers, the SIMS determined elemental boron concentration ([B]) was compared to the net carrier concentration measured using mercury-probe $C-V$. A typical epilayer grown using a Si/C = 0.51 had a $C-V$ measured net carrier concentration of $p = 5 \times 10^{15} \text{ cm}^{-3}$ as compared to a net carrier concentration of $p = 3.5 \times 10^{17} \text{ cm}^{-3}$ for an epilayer grown using a Si/C = 0.11 in a separate experiment but with an identical reactor concentration of diborane (1.6 ppm). SIMS analysis revealed an elemental B concentration of [B] = $6.5 \times 10^{16} \text{ cm}^{-3}$ for the lower doped ($p = 5 \times 10^{15} \text{ cm}^{-3}$) epilayer and [B] $1 \times 10^{18} \text{ cm}^{-3}$ for the more highly boron-doped ($p = 3.5 \times 10^{17} \text{ cm}^{-3}$) SiC epilayer. The large increase in B incorporation resulting solely from a change in the Si/C ratio illustrates 1. the strong dependency of the B incorporation on the Si/C ratio used during epilayer growth and 2. the preferential B occupancy of the Si-site versus the C-site.¹⁾

6. Hydrogen Incorporation with Boron

6.1 Low temperature photoluminescence

Hydrogen incorporation was also revealed in the B-doped Si-face and C-face epilayers via low temperature photoluminescence and by SIMS analysis [4]. Three B-doped SiC epilayers, grown using identical Si/C ratios but with different diborane concentrations, were subsequently examined using LTPL. Identical Si/C ratios were used in order to eliminate potential effects of different propane concentrations on hydrogen incorporation, thereby isolating the hydrogen incorporation effect to only the change in diborane concentration. The resulting spectra, shown in Fig. 5a, reveal that a significant amount of hydrogen was contained in each of the B-doped epilayers. The most prominent line (at 4193 Å and labelled H₃), observed both in hydrogen-ion implanted SiC [27, 28] and in CVD grown SiC epilayers [29], has been previously assigned to a hydrogen center. The H₃ line intensity increased, relative to the two N bound exciton lines (S₀ and R₀), as the $C-V$ net carrier concentration increased for the sample series $p = 2 \times 10^{15}$, 7×10^{15} , and $2 \times 10^{16} \text{ cm}^{-3}$. This correlation of increased H₃ intensity with increasing p-type character suggests that the hydrogen incorporation is directly proportional to the amount of B incorporated into the SiC epilayer.

The intensity of all hydrogen related spectra decreases after the samples are subjected to a 1700 °C anneal in argon for 0.5 h (see Fig. 5b). In comparing the results shown in Fig. 5b with those of a, it becomes evident that the H₃ line intensity has severely decreased relative to S₀, a nitrogen bound exciton line. This indicates that either most of the hydrogen has diffused out of the SiC epilayer or the optical activity of the hydrogen has been altered. Also note that lines related to the boron center in 6H-SiC, as recently published for B implanted 6H-SiC [30], were not observed before or after the high temperature anneal, which is less understood and still under investigation.

¹⁾ Note: More quantitative electrical comparison of these samples is not reliable because of the differing unintentional elemental nitrogen concentrations contained in these epilayers resulting from the relative decrease in propane concentration when changing the Si/C ratio from Si/C = 0.51 to 0.11 ($N_D = 4.5 \times 10^{16}$ versus $N_D = 5 \times 10^{15} \text{ cm}^{-3}$) combined with the uncertainty in SIMS determinations of these relatively low nitrogen concentrations.

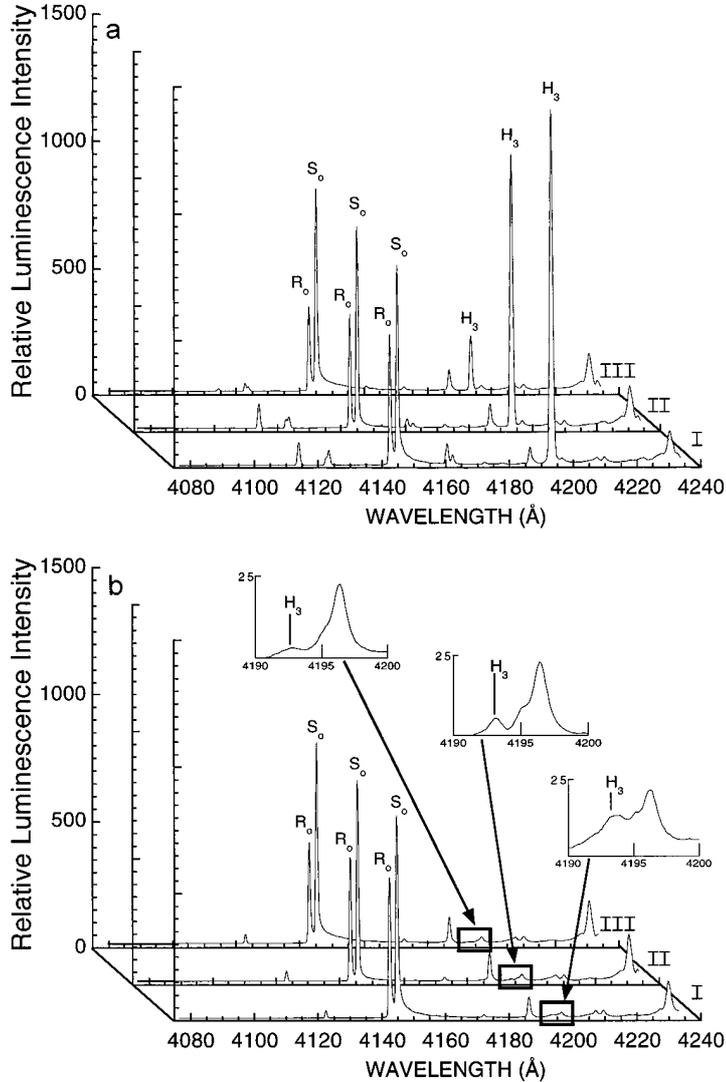


Fig. 5. a) LTPL spectra of three 6H-SiC epilayers before anneal, with decreasing hydrogen-related line intensities (labelled H_3). Corresponding to the decrease in H_3 line intensities, the samples had decreasing measured net carrier concentrations of I: $p = 2 \times 10^{16} \text{ cm}^{-3}$, II: $7 \times 10^{15} \text{ cm}^{-3}$, and III: $2 \times 10^{15} \text{ cm}^{-3}$. The LTPL spectra were normalized relative to the intensity of S_0 , one of the nitrogen bound exciton LTPL lines. b) LTPL spectroscopy of the samples after a 1700 °C anneal in argon for 0.5 h revealed a relative decrease in the intensity of the hydrogen related line (labelled H_3). The insets of the LTPL spectra from 4190 to 4200 Å illustrate that a small amount of hydrogen remained in the epilayers following the high temperature anneal

6.2 SIMS analysis for hydrogen

Epilayers containing stepped increases in B concentration [B], from only varying the Si/C ratio, were prepared as described in Fig. 6 and subsequently analyzed for hydrogen using

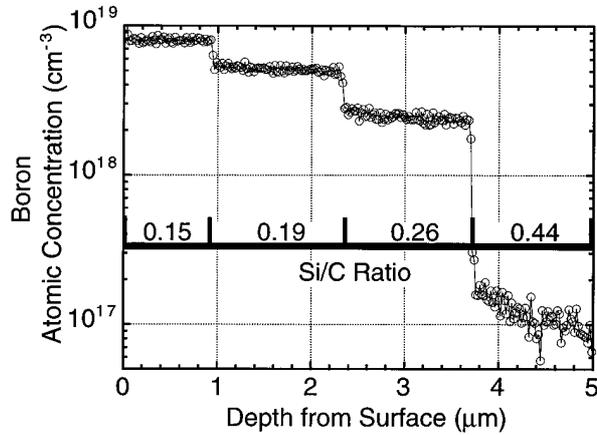


Fig. 6. The SIMS determined atomic boron concentration increased as the Si/C ratio was decreased by changing only the propane flow (stepwise in 10 sccm increments from 15 sccm to 45 sccm) while maintaining a constant silane (20 sccm) and diborane (50 sccm) flow during the CVD 6H-SiC epilayer growth

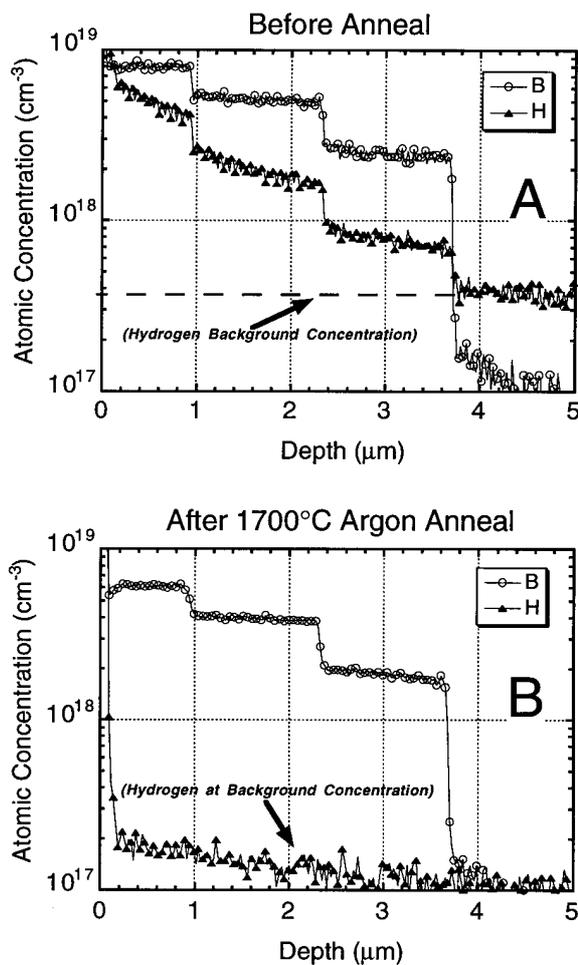
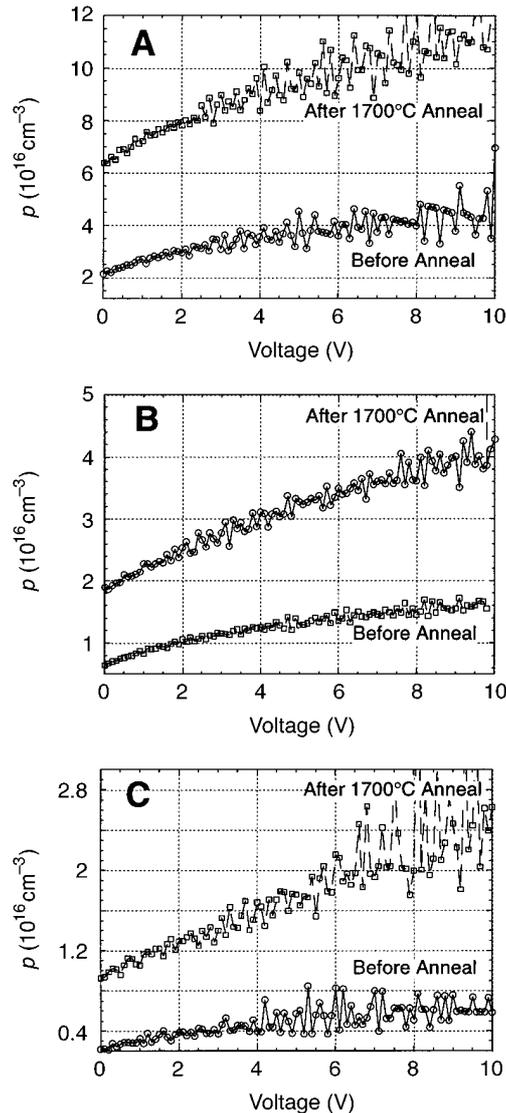


Fig. 7. A) SIMS analysis of a boron-doped, Si-face SiC epilayer revealed that prior to anneal the hydrogen concentration increased as the boron concentration increased within the CVD SiC epilayer. B) SIMS analysis after an anneal in argon at 1700 °C (0.5 h) revealed that the hydrogen concentration is at or below the H-detection limit of the SIMS instrument, indicating the outdiffusion of hydrogen during the high temperature anneal. Also, no significant solid state diffusion of boron was detected, as evidenced by the continued sharpness of the boron concentration profile

SIMS. This was done to 1. confirm that hydrogen and B incorporation are related and 2. determine whether the hydrogen was removed or if its optical activity was simply altered as a result of the 1700 °C anneal. The results of SIMS analysis of the [B]-stepped epilayer, prior to the high temperature anneal, are displayed in Fig. 7A. The increase in hydrogen concentration is observed to correspond with the increase in B concentration



within the epilayer. This indicates that the hydrogen incorporation is directly related to the B incorporation in the 6H-SiC epilayers. It is not known whether the hydrogen atom is substitutional or defect related [31] as was previously reported for hydrogen in other semiconductor materials (the hydrogen concentration profile displayed in Fig. 7A is artificially less than the B concentration and each step in the hydrogen concentration profile also contains a downward slope, both of which are artifacts of the SIMS measurement.²⁾

After a 1700 °C anneal for 0.5 h in argon, the sample was again SIMS depth profiled for determination of B and hydrogen concentration. The results are displayed in Fig. 7B which indicates that the hydrogen has diffused out of the SiC epilayer as a result of the 1700 °C anneal. The amount of hydrogen remaining within the B-doped epi-

Fig. 8. The C - V measured net carrier concentrations before (lower plot in each graph) versus after (upper plot) at 1700 °C anneal indicates more than a threefold increase in the net carrier concentration for all three doping levels. Identical Si/C ratios (0.44) were used during the epilayer growth in order to minimize potential effects of different propane concentrations on hydrogen incorporation. The diborane flows were A) 35, B) 26, and C) 24 sccm

²⁾ Note: This can be explained by considering that lower mass elements are more affected by the geometric effects of deep craters (i.e. greater than 6 μm sputter-depth) and that the resulting field perturbations “scatter” the lower mass ions more readily than the relatively heavier ions (e.g. in comparing B(+C)- to H-signals as a function of sputter depth).

layer is below the hydrogen background concentration ($< 2 \times 10^{17} \text{ cm}^{-3}$) in the SIMS instrument. Also, it is interesting to note that B does not seem to undergo appreciable solid state diffusion as a result of the 1700°C anneal, which is evidenced by the continued sharpness of the [B]-profile displayed in Fig. 7B.

6.3 Hydrogen passivation of acceptors

A significant concentration of hole-passivating hydrogen is also incorporated during the growth of the B-doped epilayer. To determine the extent of hydrogen passivation of dopants, the sample series discussed in Fig. 8 was examined using mercury-probe C - V before and after a high temperature anneal in argon. The C - V results after a 1700°C anneal, versus before the anneal, indicate a three- to fourfold increase in the net carrier concentration for all three doping levels (see Fig. 8). This increase indicates that, prior to the anneal, hydrogen was passivating the acceptor atoms of the B-doped SiC epilayers. The amount of hydrogen-passivated acceptors was estimated for each sample by a comparison of the measured net carrier concentration (at $V = 0$) before and after the 1700°C anneal. The increase in carrier concentration, due to the reduction in hydrogen-

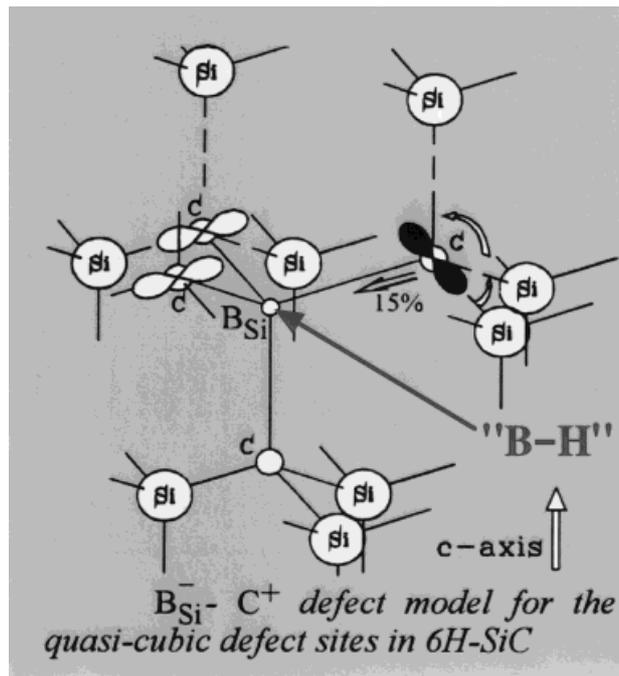


Fig. 9. After Reinke et al. [26] in which they propose that B substitute into a Si-site and that the hole resides on an adjacent C atom p-orbital as a result of an electron transfer from the adjacent C to the B atom. The "B-H" species is now proposed as the source of the hole-passivating H which is simultaneously incorporated into the growing B doped CVD epilayer. In this way, the H could be considered to passivate the B, thereby preventing the formation of a hole by interfering in the electron transfer process from the adjacent C to the B atom. This transfer could then be enabled by the removal of H from the crystal via the high temperature anneal, consistent with post-anneal C - V measurements

passivation with post-anneal, was approximately $4.5\times$, $3\times$, and $3.25\times$ for the three samples with post-anneal net carrier concentrations of $p = 9 \times 10^{15}$, 1.9×10^{16} , and $6.5 \times 10^{16} \text{ cm}^{-3}$, respectively [4].

By using atomic size as a first approximation to explain the preference for B incorporation into the Si-site (i.e. by neglecting chemical bonding arguments), the nonpolar covalent radii for the elements of interest are: Si (1.17 Å); C (0.77 Å); and B (0.82 Å); [22]. The more closely matched atomic size of B to C suggests that B should substitute mainly for C in the C-sites, which is in direct conflict with experimental evidence [4, 32]. However, a considerable amount of hole-passivating hydrogen is simultaneously incorporated into the growing B doped CVD epilayer and therefore a “B–H” species could be considered as the substitutional species. In this case, a “B–H” species would have a size ($\approx 1.10 \text{ Å}$) more closely matched with that of Si (1.17 Å) and therefore should occupy a Si-site, in agreement with the experimental results. Because this is only a first approximation, it does not imply that B substitutes exclusively into the Si-sites but rather that Si-site substitution is favored because of the larger effective size of the proposed “B–H” species.

This rationale is also consistent with the results reported by Reinke et al. [26] in which they propose that B substitutes into a Si-site and that the hole resides on an adjacent C atom as a result of an electron transfer from an adjacent C to the B atom. The H atom could be considered to passivate the B, thereby preventing the formation of a hole by interfering in the electron transfer from the adjacent C to the B atom (see Fig. 9). This transfer could then be enabled by the removal of hydrogen from the crystal via the high temperature anneal which is consistent with the C - V measured three-fold increase in net hole concentration as previously discussed above.

7. Nitrogen Doping

In contrast to the similar doping results on the C-face and Si-face for the other three dopants, N doped epilayers on the 6H-SiC(000 $\bar{1}$) C-face revealed a more complex response of N incorporation with a change in the Si/C ratio. As shown in Fig. 10, the SIMS determined atomic N concentration contained in the C-face epilayer initially decreases as the unintentional background nitrogen in the CVD system slowly decreases during the start of epilayer growth. The N incorporation then decreases as the propane flow is decreased (from 50 to 15 sccm), which is directly opposite to the site-competition effect for the Si-face epilayers. It is important to note that the (C-face) N incorporation decreases despite the simultaneous introduction of 100 sccm of nitrogen into the CVD reactor, which demonstrates the dominant effect of the Si/C ratio on dopant incorporation. As the propane flow is subsequently increased stepwise, the C-face N incorporation initially increases from 3×10^{18} to $6 \times 10^{19} \text{ cm}^{-3}$ and then decreases stepwise to $3 \times 10^{19} \text{ cm}^{-3}$, coinciding with the stepwise increases in propane flow.

The N doping on the Si-face is consistent with the proposed site-competition mechanism, in which the relatively small N atoms compete with C atoms for available C-sites. However, the results from using site-competition epitaxy on the C-face are not as easily understood. SIMS analysis of N-doped C-face epilayers indicate that N-incorporation initially increases with increasing propane flow. This increase in N-incorporation for the C-face reaches a maximum and subsequent increases in propane flow result in a decrease in N-incorporation, which is similar to site-competition for Si-face epilayers.

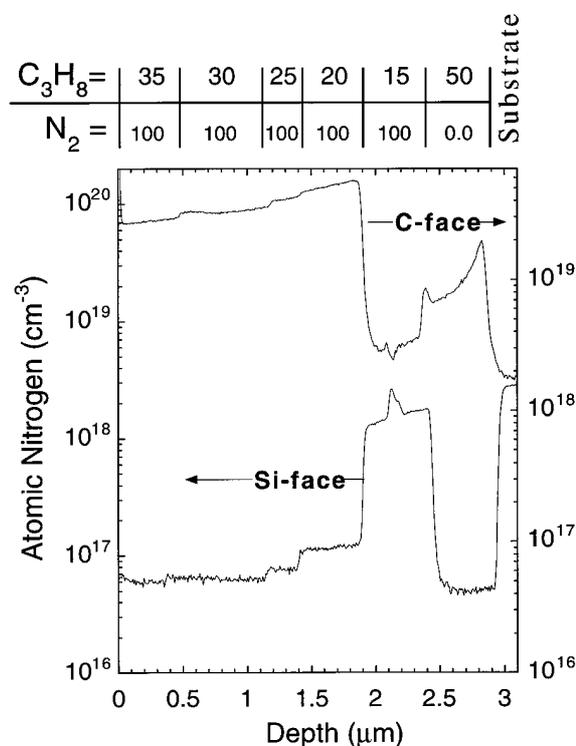


Fig. 10. SIMS depth profile of a C-face compared to a Si-face 6H-SiC(0001) N-doped epilayer grown during the same growth run. Note that the (C-face) N incorporation decreases, as the propane flow decreases (from 50 to 15), despite the simultaneous introduction of 100 sccm of nitrogen into the CVD reactor, which demonstrates the dominant effect of the Si/C ratio on dopant incorporation. Subsequent propane flows were varied, from 15 to 35 (sccm), to change the Si/C ratio and effectively control N incorporation with constant nitrogen (100 sccm) and silane (20 sccm) flows

This can be understood by considering the relatively small size of the N atom (0.74 Å) which would allow possible substitution into both the C-site and the Si-site. For example, in Fig. 10 the Si-face substrates have very low unintentional (i.e. at $N_2 = 0$ sccm) N-dopant incorporation when grown in excess propane ($C_3H_8 = 50$ sccm) at the start of the epilayer growth. In contrast, the C-face 6H-SiC epilayer initially demonstrated a large amount of unintentional N incorporation (also at $C_3H_8 = 50$ sccm). The propane flow was then decreased ($C_3H_8 = 15$ sccm) resulting in a decreased N incorporation for the C-face despite the simultaneous introduction of nitrogen (100 sccm). This is consistent with N mainly occupying the Si-sites on the C-face. As the propane flow was then increased, as shown in Fig. 10 ($C_3H_8 = 20$ sccm), the N-dopant incorporation increases for the C-face which is consistent with N substituting into Si-sites. However, further stepwise increases in propane flow (in excess of 20 sccm) appears to reverse this effect for the C-face, resulting in a stepwise decrease in N-dopant incorporation (for $C_3H_8 = 25$ to 35 sccm) which is consistent with the excess C competing with N for the C-sites.

These results of using site-competition on the C-face are consistent with the N-dopant atoms preferentially substituting into the Si-sites for propane flows less than 20 sccm. As the propane flow is then increased further from $C_3H_8 = 20$ to 35 sccm, the decrease in SIMS-determined N incorporation is more consistent with N substitution into the C-sites, which is similar to the Si-face results. Work is continuing to further elucidate the site-competition mechanism on both the Si-face as compared to the C-face of SiC.

8. Conclusion

Site-competition epitaxy has been successfully used for p-type and n-type dopant control on both the Si-face and C-face of 6H-SiC(0001) off-axis substrates. The doping results for the C-face provides supporting evidence that the site-competition effect is highly dependent on the SiC polarity but not significantly affected by the polytype. The results for both the 6H- and 4H-SiC Si-face samples were similar whereas the 6H-SiC C-face samples yielded significantly different results, most dramatically for N-doped epilayers. It also becomes obvious, in comparing the results from simultaneous growth of N-doped epilayers on the C-face and Si-face, that the site-competition mechanism is dominated by surface chemistry of the SiC substrate and relatively less on gas phase interactions.

For p-type doping, the Al and B dopant incorporation increased as the Si/C ratio was decreased by increasing the propane flow on both polar faces. Similarly, the P dopant incorporation also increased on both the Si-face and C-face as the Si/C ratio was intentionally decreased from either a decrease in the silane flow or increase in the flow of propane during epilayer growth. This is consistent with the P, Al, and B competing with Si for the available Si-sites.

The apparent site preference for each dopant can be partially rationalized by considering their atomic sizes relative to the sizes of Si (Si-site) and C (C-site). Here, the P and Al atoms are clearly too large for incorporation into the C-site without significantly distorting the lattice spacing, whereas B needs further explanation. Because a significant amount of H is incorporated with B we must consider the relative size of B to possibly be of a “B–H” species. For this situation, the effective size of the “B–H” species is also too large and will not easily fit into the C-sites without significantly altering the SiC lattice dimensions. In contrast, the relatively small size of the N dopant atom theoretically allows incorporation into either of the lattice sites. Therefore, it is now proposed that N doping on the Si-face could result in N incorporation into both the Si-site and the C-site, with N potentially having a preferred incorporation into the C-site. In contrast, for N doping on the C-face, N appears to mainly incorporate into Si-sites with relatively less incorporation into C-sites. Therefore, the originally proposed site-competition mechanism needs modification to possibly account for N dopant incorporation into both Si-sites and C-sites, in which the degree of incorporation for each site (i.e. Si-site versus C-site) could be dependent upon the growth surface polarity (i.e. Si-face or C-face).

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